

UTILIZATION OF WASTE

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UTILIZATION OF TECHNOGENIC MATERIAL FROM AN OIL-PROCESSING COMPANY IN THE PRODUCTION OF BUILDING CERAMICS

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The results of studying the possibility of using a technogenic material (catalyst) in the production of building ceramics are discussed. The physicochemical properties and structural parameters of ceramic samples are given. In the case of introducing the catalyst in a molding mixture, the firing temperature should be increased and the amount of the catalyst should not exceed 7–10%.

The production of building materials involves large-scale consumption of natural resources. This consumption of natural materials can be decreased, thus contributing to environmental protection, by replacing natural minerals by technogenic materials and industrial waste [1, 2].

The problem of utilization of industrial waste is topical, but the level of recycling technogenic materials remains low. The fact is that industrial waste frequently has a heterogeneous chemical composition, and some kinds of waste are highly toxic. The use of byproduct frequently lowers the properties of building materials and requires additional production expenses, which raises the end cost of the product.

The oil-processing sector is a strategically important sector of industry. Oil-processing companies satisfy 42% of energy demands of the European Union and produce 95% of fuel. However, processing vast volumes of raw materials generates byproducts or waste, whose quantities are increasing. These wastes keep taking up enormous areas for dump-

ing grounds and create a threat of additional pollution of the ambient medium. The types of waste currently generated by oil-processing plants are mainly slime and waste chemical reagents, such as different catalysts, acids, etc.

European manufacturers use waste catalysts in the production of cement clinker or asphalt-concrete. The authors of [3] proposed adding catalysts to refractory concrete. The authors of [4] proposed using oil-processing waste in the production of main ceramic materials: facade bricks, construction blocks, roof tiles. It has been established that such additive has a negative effect on the compressive strength of products.

The purpose of our study is to investigate the possibility of using a waste catalyst catalytic cracking catalyst from the Mazheiku-Nafta oil-processing plant (Lithuania) in the production of building ceramics. The utilization of this waste is especially topical in the context of environmental protection, considering that it contains heavy metal ions.

We used illite-bearing clays of two types [5] from the deposits of the Devonian (clay A) and Quaternary (clay B) periods, grog additives represented by sand and chamotte, and

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TABLE 1

Material	Weight content, %													calcination loss
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	MnO	K ₂ O	Na ₂ O	MoO ₃	P ₂ O ₅	NiO	ZnO	RE	
Clay:														
A	47.60	17.79	7.66	6.27	3.59	0.09	4.49	0.55	—	—	—	—	—	11.50
B	66.33	15.80	6.42	1.80	2.72	—	1.63	—	—	—	—	—	—	5.30
Catalyst	—	68.85 – 85.25	—	—	—	—	—	0.15	10.00 – 13.00	2.00 – 6.00	2.00 – 4.00	0.10 – 4.00	0.50 – 4.00	—

TABLE 2

Molding mixture	Weight content, %				
	clay A	clay B	sand	chamotte	catalyst
1	20	60	15	5	—
2	16	60	12	5	7
3	15	65	10	—	10
4	10	60	5	5	20

the waste catalyst generated in catalytic cracking. The chemical composition of the initial argillaceous components and the catalyst are listed in Table 1.

Clays A and B are clays with a small sintering interval (30–70°C). X-ray phase analysis using a DRON-2 diffractometer indicates that the crystal structure of clays A and B consists of hydromica, chlorites, kaolinite, quartz, feldspar, dolomite, calcite, and hematite. Clay B is contaminated by large carbonate inclusion and is classified as acid or semiacid clay, although in general this amount is lower than in clay A.

The catalyst consists of granules of diameter 1.3–1.5 mm containing oxides of aluminum, molybdenum, nickel, phosphorus, zirconium, sodium, and rare-earth elements (RE). The bulk density of the catalyst is at least 0.80 g/cm³.

The x-ray phase analysis of sand indicates that its crystal structure is made up of quartz, feldspar, and dolomite. The granulometric composition of sand is represented by fine particles of size below 2.5 mm; among them particles of size below 0.315 mm prevail (on the whole more than 70%).

The diffraction patterns of the catalyst fired at 1000°C exhibits lines testifying to the presence of alumina γ -Al₂O₃: 4.13, 3.45, 2.79, 2.40, 1.98, and 1.40 Å.

In our experiments, the argillaceous components and sand were dried to a constant weight, milled in a jaw crusher, and sifted through a No. 063 sieve. Chamotte was similarly dried and milled and then sifted through a No. 0315 sieve. The catalyst was milled using a disintegrator.

The compositions of molding mixtures are listed in Table 2; the quantity of the catalyst in the batch varied from 0 to 20%.

A mixture prepared for molding matured for 3 days in a moist state. After that samples were produced by plastic molding in order to investigate their main properties, structural parameters, and compressive strength.

The preliminary drying of samples was performed at room temperature and then for 2 days in a drying cabinet at a temperature of 110 ± 5°C. The firing of molded samples was performed in an electric furnace with automatic temperature control (± 1°C) at the maximum temperatures of 1050, 1100, and 1150°C with an isothermal exposure for 4 h.

The physicomachanical properties and structural parameters of the samples were determined. The total shrinkage S_h and density of ceramic samples ρ were determined according to LST 1272–92 and the compressive strength R_c was found according to LST EN 772-1:2003. The structural parameters, such as water absorption with exposure in water

for 72 h W_{72} , effective and total porosity W_e and W_p , pore space reserve P_p , conventional thickness of pore and capillary walls D , and the degree of structural heterogeneity of samples H were calculated based on the following formulas:

$$W_{72} = \frac{m_1 - m_0}{m_0} \times 100;$$

$$W_e = \rho \frac{m_1 - m_0}{m_0} \times 100;$$

$$W_p = \rho \frac{m_3 - m_0}{m_0} \times 100;$$

$$P_p = 1 - \frac{W_e}{W_p} \times 100;$$

$$D = \frac{100 - W_p}{W_p};$$

$$H = \frac{h_{\max} - h_{\min}}{h_{\text{av}}},$$

where m_0 is the weight of the sample dried to a constant weight, g; m_1 is the weight of the sample after its exposure in water for 72 h, g; ρ is the sample density, g/cm³; m_3 is the weight of the sample after vacuum treatment and exposure in water for 24 h, g; W_e and W_p are the effective and total open porosity, %; h_{\max} , h_{\min} , and h_{av} are, respectively, the maximum, minimum, and average velocity of the capillary wetting front along the sample molding direction, cm/h.

The effective porosity characterizes the quantity of effective open pores and capillaries. In the technological aspect, this parameter also indicates the degree of sintering of the material. To estimate the heterogeneity of the structure, we use the parameter P_p , which mainly characterizes the reserve (free from water) in the pore space. The total open porosity also indicates the sintering of the material and at the same time is used to calculate the conventional thickness of the pore and capillary walls. It should be noted that the total open porosity parameter does not reflect the quantity of sealed pores and capillaries. Since the heterogeneity of the structure is very significant for ceramic products (this property is especially important for prevailing pores and capillaries oriented in the molding direction), it is estimated by the parameter H , which makes it possible to estimate heterogeneities based on their conventional length.

The mean values of the specified parameters are listed in Table 3.

All obtained results were subjected to preliminary statistical analysis. For instance, the histogram of the reserve porosity parameter (Fig. 1) indicates its normal distribution in ceramic samples, both with and without a catalyst additive.

The maximum reserve porosity was registered in molding mixture 3 fired at 1150°C. The variation interval of this

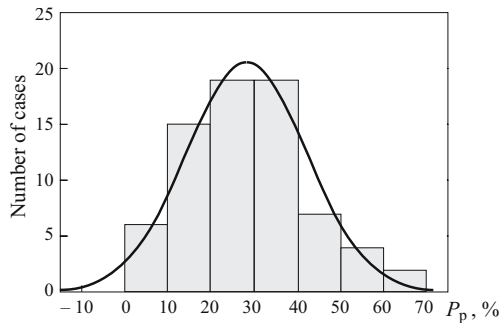


Fig. 1. Histogram of reserve porosity P_p of ceramic samples.

parameter ranges from 42.95 to 60.93%. Based on the above data, it can be assumed as well that these samples have the highest frost resistance in service.

It follows from the above data (Table 3) that as the temperature increases, the density and strength of the samples grow and their water absorption decreases. This also leads to a decrease in the effective and total open porosity of the samples and points to the intensified sintering of ceramic mixtures. At the same time, the conventional thickness of the pore and capillary walls grows, and the reserve space porosity and the degree of structural heterogeneity increase. One can presumably expect as well enhanced frost resistance of ceramic samples in service.

Upon introducing 7 and 10% catalyst into the molding mixtures (mixtures 2 and 3), as well in the case of firing samples at the maximum temperature of 1150°C, the water absorption of samples does not exceed 6%. However, as the catalyst content increases to 20%, the water absorption grows on the average by 9.67%. In general the introduction of the catalyst additive has a negative effect on the compressive strength of samples, regardless of their firing temperatures. Thus, with a simultaneous increase in the quantity of the catalyst and the firing temperature the compressive strength of the sample may decrease by 30%.

Ceramics made of mixture 3 fired at the maximum temperature of 1150°C has the highest density (2154 kg/m³) and highest pore space reserve (51.69%). Furthermore, it has a

low effective porosity (8.31%) and its water absorption is not higher than 4%. Moreover, this ceramic has the maximum degree of structural heterogeneity (4.0), which can be attributed to intense sintering and the formation of heterogeneous pores and capillaries. Presumably, a large amount of the vitreous phase is formed in this case and the pores and capillaries in general keep getting larger. All this gives grounds to expect that ceramics made of mixture 3 may also have the maximum frost resistance in service.

The effect of the catalyst additive in molding mixtures on the properties of samples is shown in Fig. 2. It can be seen that the quantity of catalyst introduced in the mixture affects the water absorption of samples: as the amount of catalyst increases, the water absorption grows (Fig. 2a). However, if the degree of structural heterogeneity of a sample is high (4.0 – 4.5, which points to a sintered structure), the catalyst additive has virtually no effect on its water absorption, which is not higher than 6%.

Any quantity of introduced catalyst raises the effective porosity of samples (Fig. 2b). However, the minimal effective porosity is possible only with a density exceeding 2000 kg/m³.

Thus, a catalyst additive modifies the physicomachanical properties and structural parameters of ceramic samples, which is a consequence of the interaction between all components of the molding mixture under firing. X-ray phase analysis of samples made of molding mixture 1 without catalyst additives and fired at 1100°C has identified reflections corresponding to quartz, hematite, anorthite, and spinel.

X-ray phase analysis of samples based on mixtures with 10 and 20% catalyst additives (mixtures 3 and 4) clearly identifies the corundum maxima. Corundum is possibly formed due to the transformations occurring in the catalyst at higher temperatures: $\gamma\text{-Al}_2\text{O}_3$ transforms into $\alpha\text{-Al}_2\text{O}_3$. Calcium oxide contained in the clay actively reacts with molybdenum oxide, which leads to the synthesis of powellite. It is observed as well that the x-ray reflections of anorthite decrease or disappear, which is presumably related to the decreased content of the illite-bearing clay (clay A) and the increased quantity of the technogenic material introduced.

TABLE 3

Parameter	Ceramics based on molding mixtures fired at temperature											
	1050°C				1100°C				1150°C			
	1	2	3	4	1	2	3	4	1	2	3	4
Sh , %	6.14	5.42	6.17	6.42	7.73	8.42	10.17	8.99	9.57	8.53	10.31	10.71
ρ , kg/m ³	1945	1847	1866	1799	2100	2083	2048	1815	2141	2096	2154	1934
R_c , MPa	17.30	14.58	13.21	11.98	19.88	16.09	15.62	14.45	22.04	16.64	17.04	16.67
W_{72} , %	8.42	10.86	11.32	16.61	3.80	6.09	6.78	13.76	3.27	5.46	3.86	9.67
W_e , %	16.38	20.05	21.12	29.87	7.98	12.68	13.88	25.00	7.00	11.43	8.31	18.70
W_p , %	22.17	18.44	26.09	33.74	15.38	19.98	19.96	30.43	10.56	16.51	17.20	24.99
P_p , %	26.12	8.73	19.05	11.98	48.11	36.54	30.46	17.85	33.72	30.76	51.69	25.17
D	3.51	4.42	2.83	1.96	5.50	4.01	4.01	2.29	8.50	4.26	4.81	3.00
H	0.33	0.42	1.00	0.17	1.00	0.78	1.33	0.22	1.08	3.75	4.00	1.56

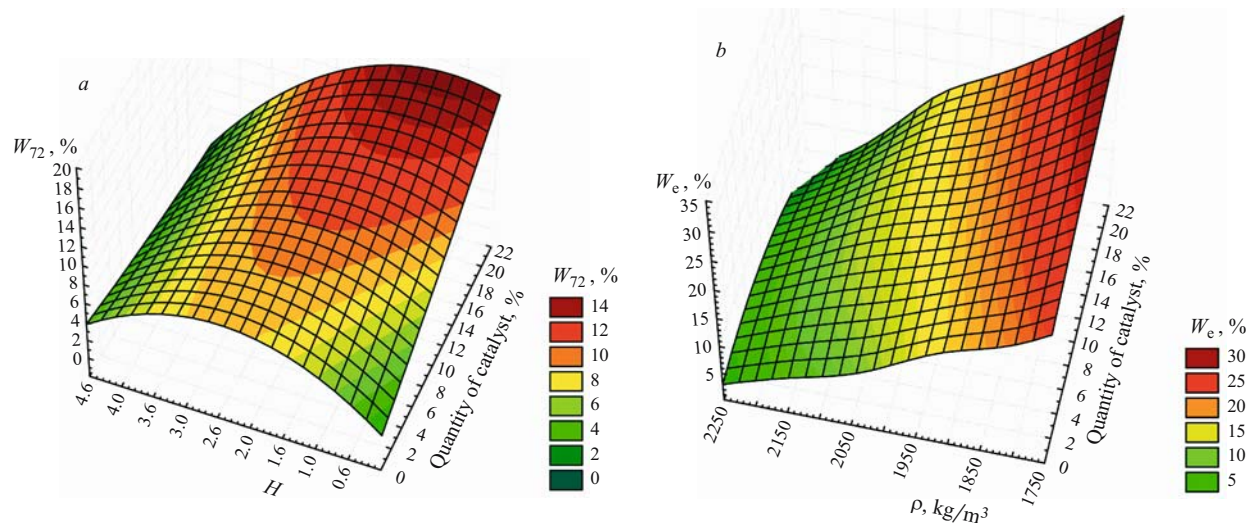


Fig. 2. The effect of the quantity of catalyst introduced in a molding mixture on water absorption W_{72} and the degree of structural heterogeneity H (a), as well as on the density ρ and effective porosity W_e (b) of samples.

The x-ray diffraction patterns of the same samples fired at the maximum temperature of 1150°C exhibit the same tendency toward the formation of corundum and powellite. Aluminum oxide contained in the catalyst actually does not react with clay minerals, as no mullite reflection has been identified in the x-ray patterns. The quantity of the introduced catalyst is manifested only in the increased intensity of the x-ray reflections of corundum and powellite.

All the above changes point to chemical reactions taking place between the batch components and the catalyst.

Preliminary investigations established that the leaching of heavy metals upon introducing the catalyst into the molding mixtures is minimal and satisfies the current standards.

Thus the particular technogenic material, namely a catalyst from catalytic cracking at the oil-processing company, can be successfully utilized in the production of building ceramics. The catalyst has a significant effect on the physico-mechanical properties and structural parameters of ceramic material and its mineralogical composition. The optimum content of the catalyst in a molding mixture is 7–10%; the introduction of more than 10% has a negative effect on all physicochemical properties and structural parameters of the samples.

The firing temperatures for molding mixtures with catalyst additives ought to be somewhat higher. This facilitates the formation of new phases in the catalyst and the synthesis of new formations as it reacts with the clay components. As a consequence, $\gamma\text{-Al}_2\text{O}_3$ in the catalyst transforms into $\alpha\text{-Al}_2\text{O}_3$.

Heavy metal ions contained in the catalyst can be fixed in steady insoluble compounds at temperatures above 1050°C in the production of building ceramics.

REFERENCES

1. N. A. Vil'bitskaya, S. P. Golovanova, A. P. Zubekhin, N. D. Yatsenko, *Steklo Keram.*, No. 4, 21–23 (2002) (*Glass and Ceram.*, **59**(3–4)).
2. G. I. Yakovlev, "Ceramic materials based on acid fluoride," *Steklo Keram.*, No. 9, 18–20 (2002) (*Glass and Ceram.*, **59**(9–10)).
3. S. Yu. Goberis and A. B. Shtuopis, "Study of refractory concrete containing oil-processing waste catalyst," *Ogneup. Tekh. Keram.*, No. 1, 19–22 (1997).
4. G. S. Souza, R. S. Santos, and J. N. F. Holanda, "Recycling of a petroleum waste in ceramic bodies," *Mater. Sci. Forum*, **418**, 743–747 (2003).
5. R. Žurauskis, R. Mačiulaitis, F. Petrikaitis, "Usability of Lithuanian fusible clay for sintered ceramic," *Civil Eng.*, **VII**(3), 191–196 (2001).